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Abstract

A modified dc-diode plating system, utilizing a metallic screen cage as a cathode and referred as SCREEN CAGE ION PLATING (SCIP), is used to deposit Ag and Au lubricating films on Si_3N_4 and SiC surfaces. When deposition is performed in Ar or N_2 glow discharge, the surface displays poor adhesive strength (<5 MPa). A dramatic increase in adhesive strength (>80 MPa) is achieved when plating is performed in a reactive 50% O_2 + 50% Ar glow discharge. The excited/ionized oxygen species (O_2^+/O^+) in the glow discharge contribute to the oxidation of the Si_3N_4 or SiC surfaces as determined by X-ray Photoelectron Spectroscopy (XPS) depth profiling. The reactively sputter-oxidized Si_3N_4 or SiC surfaces and the activated-oxidized-metastable Ag or Au species formed in the plasma cooperatively contribute to the increased adherence. As a result, the linear thermal expansion coefficient mismatch at the interface is reduced. These lubricating Ag and Au films under sliding conditions reduce the friction coefficient by a factor of 2-1/2 to 4.

Introduction

Of all the various nonoxide ceramics used in engineering applications, Si_3N_4 and SiC are the prime candidate materials specified for the manufacture of mechanical components in advanced aircraft engines. Ceramic elements such as ball bearings, valve components, piston rings and cylinder liners are increasingly being specified for engines which have to withstand severe service operating conditions such as high temperatures, loads and speeds. Si_3N_4 has emerged as the best suited ceramic material for ball bearings, because of its high strength, hardness and relatively high toughness. But before widespread use or Si_3N_4 bearings can occur, the tribological performance must be significantly improved. Since ceramics are brittle materials, the presence of surface or near surface microflows is very detrimental to their performance. Ceramic surfaces which are in sliding, rolling, or oscillating motion generate tensile stresses, which are localized near the surface. These tensile stresses interact with the surface/subsurface flaws/defects and result in microcracking and chipping of the surface, which lead to severe wear.

It has been shown that adherent, soft Ag or Au films not only reduce the coefficient of friction during sliding contact but also reduce the surface tensile stresses that contribute to crack initiation and propagation and lead to microcracking and severe wear. In solid film lubrication the foremost requirement of the soft, metallic films is strong adherence, since the degree of adherence determines the durability of the film. Inherently, Ag and Au films display poor adherence to ceramic surfaces and cannot be directly deposited. To overcome this deficiency Ti or Cr interlayers have been used,[1-3] to achieve closer compatibility by decreasing the large difference in the Coefficient of Thermal Expansion (CTE) between the film and the substrate. The general rule is that the CTE of the coating should differ by less than 25 percent from that of the substrate.[4] In the present study, the adhesion problem is solved by using the Oxygen assisted Screen Cage Ion

Plating (SCIP) process, which favorably affects the metal/ceramic interface and dramatically increases film adherence.

Concepts of Ceramic Lubrication

Since ceramics are processed from powders using sintering, hot-pressing or hot-isostatic pressing, they possess less than theoretical density. The resulting microstructures from these powder processes generally have some inherent nanoporosity. All these factors affect deformation/fracture behavior. As these ceramic surfaces come in sliding or rolling contact, high tensile stresses develop at asperities and interact with surface/subsurface flaws, thus initiating microcracks and fragmentation of the contact surface. Ceramics are weak in tension and have hardly any ductility. Thus even the slightest degree of porosity trapped within a grain is believed to be a source of failure.

Unlike metals, which yield locally when the elastic limit is exceeded, gross microfracture can occur, which is a typical wear mode for unlubricated ceramics in sliding.[7] However, the load at which microfracture occurs can be increased by Ag or Au lubricating films.

According to the adhesion theory of friction,[6,7] the frictional force, F, is proportional to the shear strength, s, and the real area of contact, A, ($F = As$) as shown in Fig. 1(a). For friction to be low, both A and s must be small. This means that the most suitable materials must have high hardness and low shear strength. However, this is not achievable with monolithic ceramics, therefore, an adherent, thin, ductile film should be interposed between the contacting surfaces as shown in Fig. 1(b).

The soft Ag and Au films shear easily and prevent opposing asperities from coming into frequent contact. This easy shear at contact interfaces produces fewer asperity/asperity interactions which result in lower friction and reduced wear. When friction is low, the magnitude of tensile stresses developing behind the moving asperities is also reduced. As a result the surficial tensile stresses that are responsible for crack initiation and propagation at the surface/subsurface are reduced. Lowering the friction coefficient significantly increases the critical load for the onset of crack initiation and formation.

Experimental Conditions

Specimens

In this investigation pure Si_3N_4 disks, 1.9 cm in diameter, and SiC square flats (1.2 cm x 1.2 cm) both with as surface finish of 0.1 μm rms, were plated with 0.2 to 0.4 μm thick Ag or Au films. Adhesion tests were performed on these coated specimens. Also, Si_3N_4 and SiC disks, 6.35 cm in diameter and surface finish of 0.2 μm rms, were coated with 1-3 μm thick Ag or Au films. The coated disks were tested under atmospheric conditions at 25 °C in a pin-on-disk tribometer.

Screen Cage Ion Plating (SCIP) of Ag and Au

The SCIP apparatus has been described in previous publications,[8,9] its schematic is shown in Fig. 2. Briefly, it consists of a dc-diode configuration. The ceramic specimen is suspended in a screen cage (either silver or stainless steel plated with gold) that functions as both an electron grid and a cathode, while the resistance evaporative source acts as an anode. In the present study three

different gas compositions, pure Ar, pure N_2, and a mixture of 50% Ar + 50% O_2 are used. The total gas pressure for the generation of the plasma is set at a constant value of 20 mtorr. Before Ag or Au plating is performed at –4 kV, 80 mA, the specimen is soaked in the selected plasma at –2 kV, 20 mA for about 2 min. Because of the high throwing power of ion plating, all surfaces of the ceramic pieces are coated.

Adhesion Tests

A commercial pull-off adhesion tester (Sebastian IV) is used to determine the adhesive strength of the Ag and Au films to the Si_3N_4 and SiC substrates. In these tests, an epoxy coated Al pin is secured with a mounting spring clip to the film and transferred to an oven for curing at 150 °C for 1 hr. After curing, the test pin with the coated specimen is inserted into the instrument and the pin is pulled with an increasing force normal to the plane of the film until failure occurs. This test is limited by the nominal strength of the epoxy, which is about 80 MPa. When the adhesion of the film to the substrate is high and it is not possible to pull the film off, the epoxy breaks first.

Friction Testing

The Si_3N_4 and SiC disks, SCIP'd in (Ar+O_2) glow discharge, were friction tested with bare Si_3N_4 and SiC pins which were hemispherically tipped with a 2.54 cm radius of curvature. The pin-on-disk testing was performed in a high temperature tribometer.[10] The tribotesting was performed under atmospheric conditions under 4.9N load at 1 m/sec (370 rpm) velocity for 30 min at 25 °C.

Results and Discussion

Adhesion and Coatings/Substrate Characterization

The adhesive pull-off tests were performed for the Ag and Au films plated in N_2, Ar, and 50% Ar + 50% O_2 plasmas on Si_3N_4 and SiC substrates at identical plating conditions. Usually, six pull-off tests were made on six separately plated specimens to determine the average adhesive strength as shown in Figs. 3(a) and (b). These results reveal that Ag and Au films plated in N_2 and Ar plasma on Si_3N_4 and SiC surface display poor adhesive strengths (<5 MPa). They can be detached by a scotch tape pull test. However, the adhesive strength is dramatically increased when the films are plated in a 50% Ar + 50% O_2 plasma. The oxygen-assisted deposition remarkably enhances the Ag and Au adhesive strength (>70 MPa) to the Si_3N_4 and SiC substrates. For the pull tests performed on specimens plated in Ar-O_2 plasma the failure occurred in the epoxy, indicating that the film adhesive strength is higher than the epoxy strength. The increased adhesive strength results clearly show that oxygen in the excited or ionized state (O_2^+/O^+) is instrumental in increasing the adhesive strength of the Ag and Au films to the Si_3N_4 and SiC substrates

Since the Si_3N_4 and SiC surfaces prior to Ag and Au deposition are exposed to the oxidizing (Ar + O_2) plasma for about 2 to 3 min, prior to plating these surfaces were analyzed by X-ray Photoelectron Spectroscopy (XPS). XPS depth profiles of SiC after Ar sputter etching in the non-oxidizing plasma and sputter etching in the (Ar + O_2) oxidizing plasma are shown in Figs. 4(a) and (b). XPS depth profiles of Si_3N_4 after Ar sputter etching and (Ar + O_2) sputter etching are shown in Figs. 5(a) and (b). These XPS depth profiles show the relative proportions of O, N, Si for Si_3N_4 and O, C, Si for SiC. From these composition profiles it is evident that the outermost Si_3N_4 and SiC layers are oxidized in the (Ar + O_2) plasma. The following surface oxidation reactions are proposed:[11,12]

(1) $Si_3N_4 \rightarrow SiO_xN_y \rightarrow SiO_2$
(2) $SiC \rightarrow SiC{:}O_x$

Further, when these oxidized Si_3N_4 and SiC surfaces are then Ag and Au plated in an Ar or N_2 plasma, the adherence is poor, but when plated in ($Ar + O_2$) plasma, the adherence is >70 MPa as shown in Figs. 3(a) and (b). The poor adherence of Ag and Au plated in Ar or N_2 plasma on the oxidized Si_3N_4 and SiC surfaces indicates that Ag and Au evaporated species in the Ar or N_2 plasma are transported unreacted to the oxidized surfaces. However, when Au and Ag are evaporated in the ($Ar + O_2$) plasma, it has been reported[13,14] that Au and Ag undergoes a reaction to form a metastable gold oxide Au_2O_3 or silver oxide Ag_2O on the surface. A reaction of the depositing Au or Ag species within the oxidizing plasma lead to a reactive deposition of a metastable-oxide compound which favorably affects the nucleation and interface formation. The CTE mismatch as shown in Table 1 between the noble metals and the carbides and nitrides should be reduced due to the reactively sputter-oxidized Si_3N_4 and SiC surfaces and the oxidized-metastable Ag and Au compound formation during deposition. And further, the activated-oxidized-metastable Ag and Au species may more effectively "wet" the oxidized surface due to an increased contact area.[15]

Friction Testing

The pin-on-disk friction results of oxygen assisted SCIP'd Ag and Au films run at a atmospheric conditions under 4.9 N load at 1 m/min (370 rpm) sliding velocity for 30 min at 25 °C are tabulated in Figs. 6(a) and (b). Unlubricated Si_3N_4 and SiC disks displayed high friction coefficient of 0.72 and 0.85 respectively. The Au SCIP'd films on Si_3N_4 and SiC surfaces displayed the lowest friction coefficients of 0.15 and 0.19 respectively. The Ag SCIP'd films on Si_3N_4 and SiC displayed a coefficient of friction of 0.30 and 0.38 respectively. Thus the Au films reduced the coefficient of friction by a factor of 4, whereas the Ag films reduced it by a factor of 2.5

Conclusions

1. The Screen Cage Ion Plating (SCIP) process enables one to plate metals on electrically nonconductive ceramics (Si_3N_4, SiC) with a three-dimensional coverage.
2. A dramatic increase in Ag or Au film adherence to Si_3N_4 and SiC surfaces is achieved when SCIP is performed in a reactive 50%O_2 + 50%Ar glow discharge.
3. Oxidation transformed Si_3N_4 and SiC surfaces and the formation of activated-oxidized-metastable Ag and Au species in the glow discharge should cooperatively contribute to the excellent film adherence.
4. The thermal expansion mismatched between the film and substrate should be reduced at the interface.
5. The Ag and Au plated films on Si_3N_4 and SiC surfaces reduce the sliding friction coefficient by a factor of 2-1/2 to 4.

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Table 1.—Linear Thermal Expansion Coefficients
(α) x10^{-6} °C^{-1}

Al_2O_3–7.1
Si_3N_4–3.1
SiC–4.5
Ag–19.6
Au–14.2

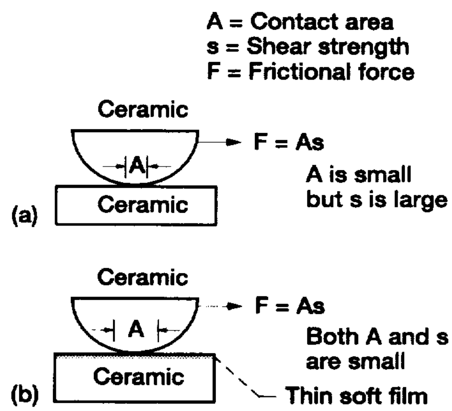

Fig. 1.—Principles of thin film lubrication.

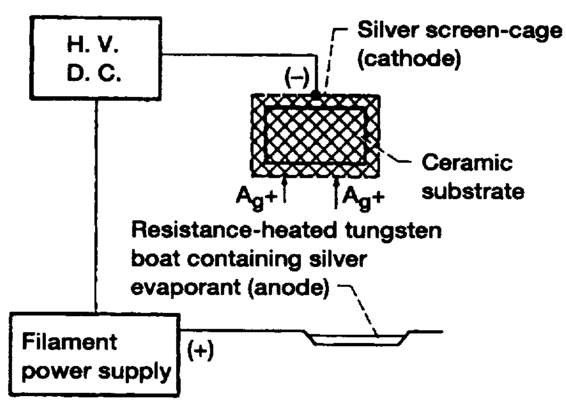

Fig. 2.—Schematic for screen cage ion plating of ceramics.

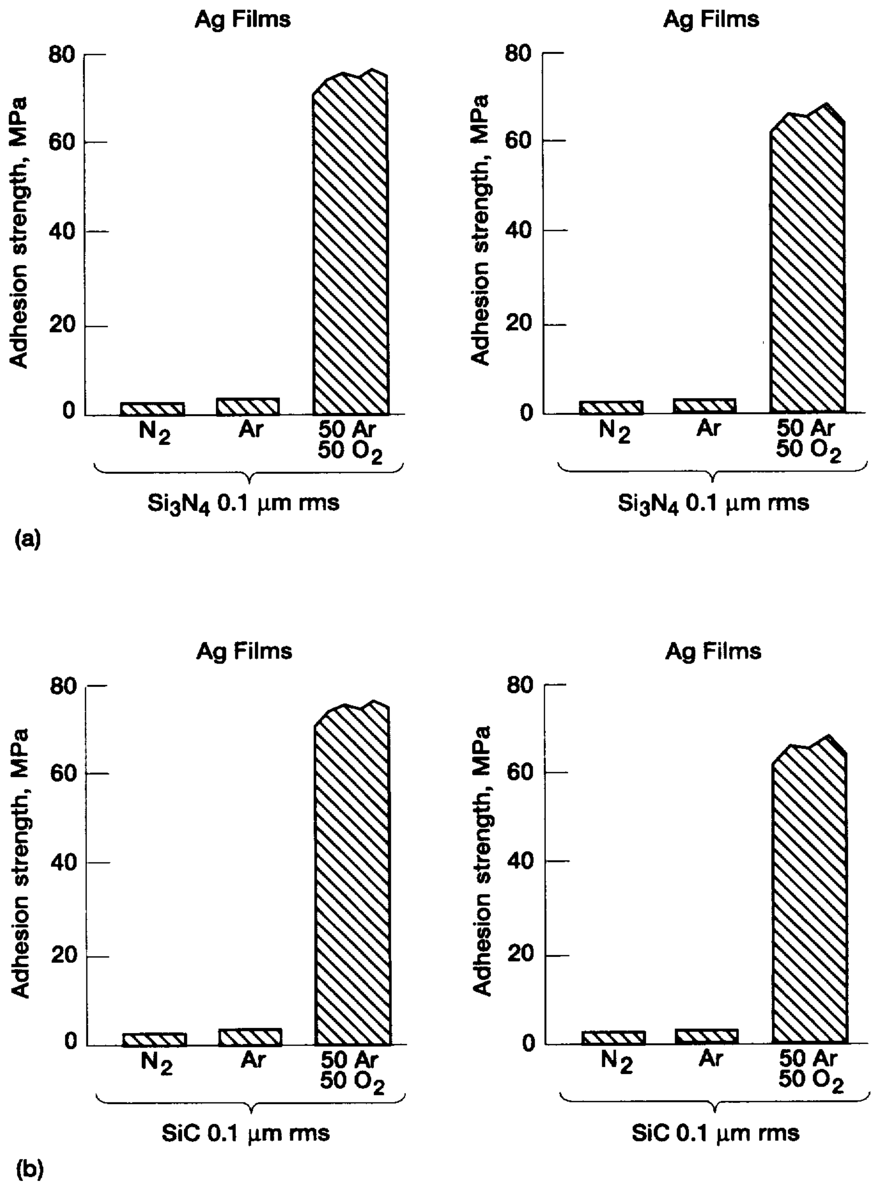

Fig. 3.—Adhesion strengths of SCIP'd Ag and Au films at different plasma compositions: (a) on Si_3N_4; (b) on SiC.

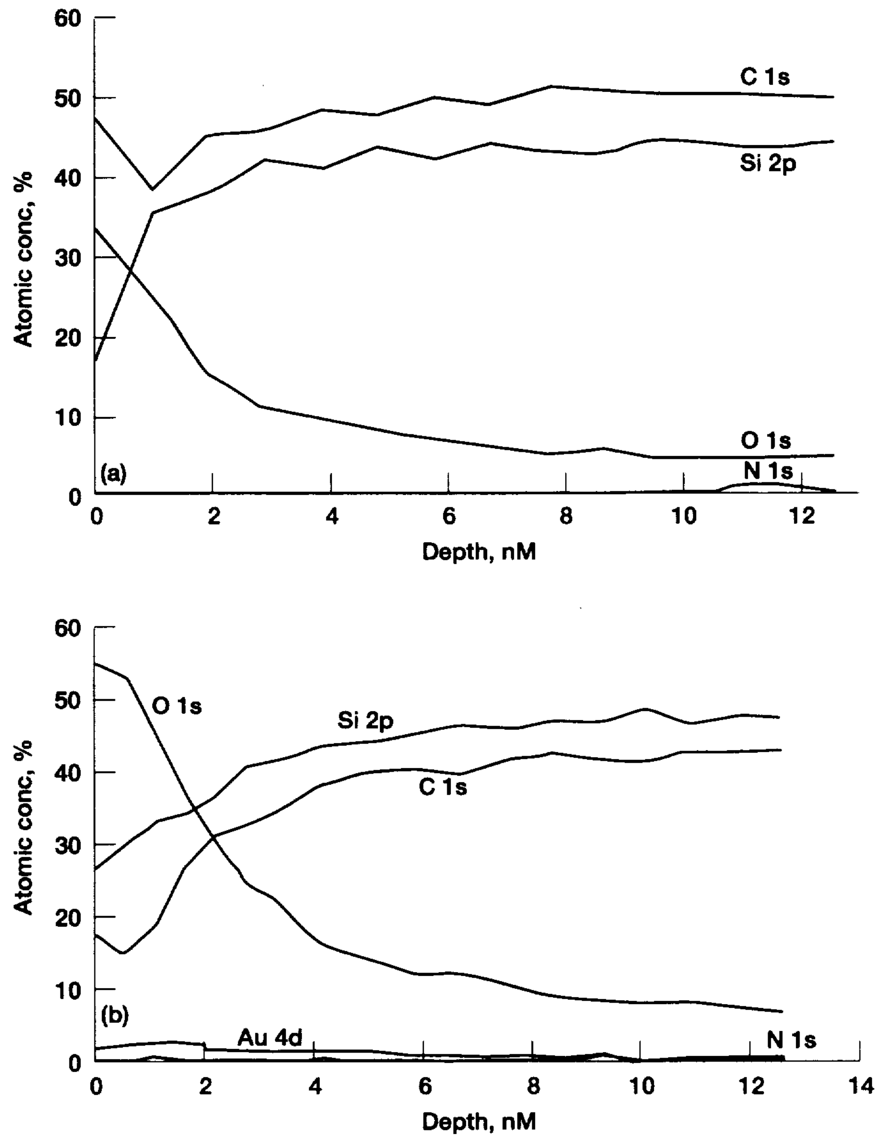

Fig. 4.—XPS depth profiles of SiC after argon and after an oxygen sputter etch in Screen cage: (a) Ar etch; (b) (Ar + O_2) etch.

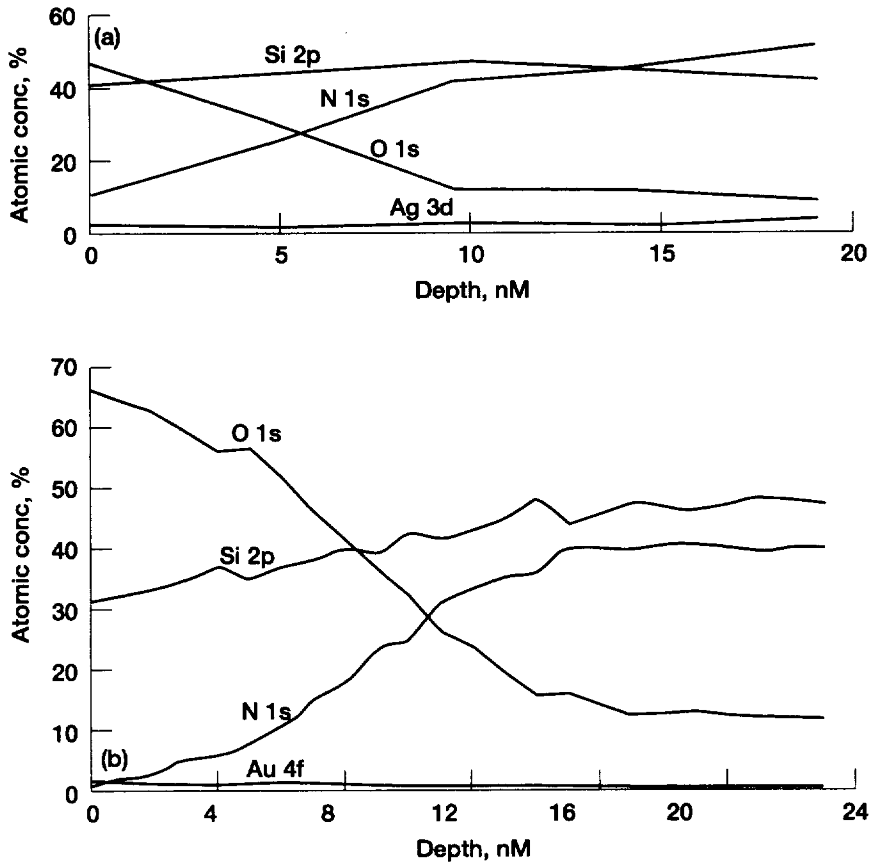

Fig. 5.—XPS depth profiles of Si_3N_4 after argon and after argon/oxygen sputter etching in screen cage: (a) Ar etch; (b) ($Ar + O_2$) etch.

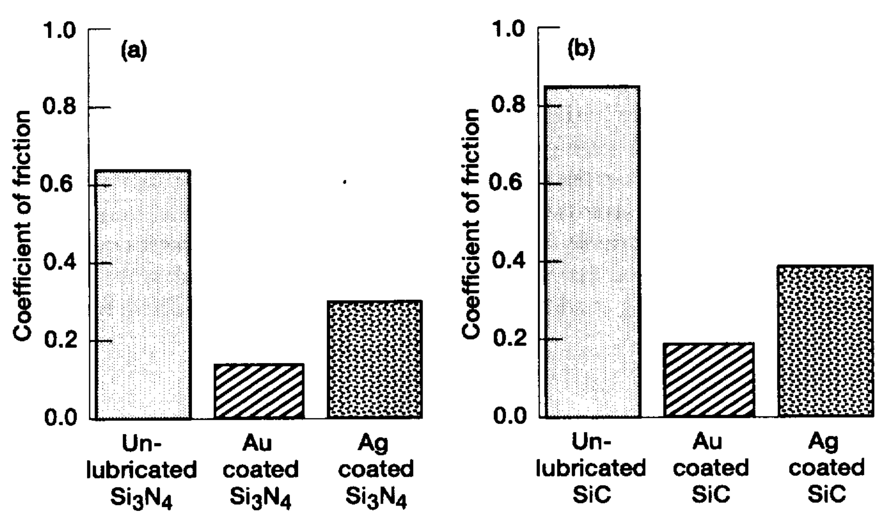

Fig. 6.—Friction coefficient of Ag and Au reactively SCIP'd films: (a) on Si_3N_4 substrates; (b) on SiC substrates.

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13. ABSTRACT (*Maximum 200 words*)

A modified dc-diode plating system, utilizing a metallic screen cage as a cathode and referred as SCREEN CAGE ION PLATING (SCIP), is used to deposit Ag and Au lubricating films on Si_3N_4 and SiC surfaces. When deposition is performed in Ar or N_2 glow discharge, the surface displays poor adhesive strength (<5 MPa). A dramatic increase in adhesive strength (>80 MPa) is achieved when plating is performed in a reactive 50% O_2 + 50% Ar glow discharge. The excited/ionized oxygen species (O_2^+/O^+) in the glow discharge contribute to the oxidation of the Si_3N_4 or SiC surfaces as determined by X-ray Photoelectron Spectroscopy (XPS) depth profiling. The reactively sputter-oxidized Si_3N_4 or SiC surfaces and the activated-oxidized-metastable Ag or Au species formed in the plasma cooperatively contribute to the increased adherence. As a result, the linear thermal expansion coefficient mismatch at the interface is reduced. These lubricating Ag and Au films under sliding conditions reduce the friction coefficient by a factor of 2-1/2 to 4.

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